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(21) International Application Number: PCT/US98/17556 (22) International Filing Date: 25 August 1998 (25.08.98) (30) Priority Data: 09/058,420 9 April 1998 (09.04.98) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: JING, Naiyong; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). NAM, Sehyun; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: BURTIS, John, A. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: MULTI-LAYER COMPOSITIONS COMPRISING A FLUOROPOLYMER (57) Abstract <p>This invention provides a method of bonding substantially non-fluorinated polymeric material to dissimilar polymers, particularly fluoropolymer materials, utilizing a bonding composition comprising substantially non-fluorinated polymeric material comprising a blend of carboxyl, anhydride, imide, or oxycarboxy functional polyolefin with a suitable organic or inorganic base and an organo-onium compound that is stable in the presence of the base. Multi-layer articles and composite constructions, including retroreflective sheeting, fuel line hoses, and adhesive articles made of a fluoropolymer layer and a substantially non-fluorinated layer are also provided.</p>		

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Multi-Layer Compositions Comprising a Fluoropolymer

FIELD OF THE INVENTION

The invention relates to multi-layer constructions comprising a fluoropolymer and a substantially non-fluorinated polymeric material as well as to methods of producing such constructions and materials. In another aspect, this invention relates to methods of improving the adhesion between a fluoropolymer and other dissimilar materials, including polyolefins. In yet another aspect, the invention relates to bonding compositions useful to adhere two dissimilar polymeric materials.

BACKGROUND OF THE INVENTION

Fluorine-containing polymers (*i.e.*, fluoropolymers or fluorinated polymers), are an important class of polymers that include, for example, fluoroelastomers and fluoroplastics. Among this broad polymer class are polymers of high thermal stability, polymers exhibiting chemical (and solvent) resistance, and polymers exhibiting usefulness along a broad spectrum of temperatures. Many of these polymers also are almost totally insoluble in a wide variety of organic solvents; see, for example, F.W. Billmeyer, Textbook of Polymer Science, 3rd ed., pp. 398-403, John Wiley & Sons, New York (1984).

Fluoroelastomers, particularly the copolymers of vinylidene fluoride with other ethylenically unsaturated halogenated monomers such as hexafluoropropylene find particular utility in high temperature applications, such as in seal gaskets and linings. See, for example, Brullo, R.A., "Fluoroelastomer Rubber for Automotive Applications," Automotive Elastomer & Design, June 1985, "Fluoroelastomers Seal Up Automotive Future," Materials Engineering, October 1988, and "Fluorinated Elastomers," Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., Vol. 8, pp. 500-515, John Wiley & Sons, New York (1979).

Fluoroplastics, particularly polychlorotrifluoroethylene, polytetrafluoroethylene, copolymers of tetrafluoroethylene and hexafluoropropylene, and poly(vinylidene fluoride), have numerous electrical,

mechanical, and chemical applications. Fluoroplastics are useful, for example, as wire coatings, electrical components, seals, and in solid and lined pipes and piezoelectric detectors. See, for example, "Organic Fluorine Compounds," Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 11, pp. 20, 21, 32, 33, 40, 41, 48, 50, 52, 62, 70, and 71, John Wiley & Sons, New York (1980).

Multi-layer constructions containing a fluorinated polymer enjoy wide industrial application; multi-layer fluoropolymer constructions find utility in, for example, fuel line hoses and related containers and in retroreflective sheeting materials. Increased concerns with evaporative fuel standards give rise to a need for fuel system components that have increased barrier properties to minimize the permeation of fuel vapors through automotive components including fuel filler lines, fuel supply lines, fuel tanks, and other components of the engine's fuel system control system. Various types of constructions have been proposed to address these concerns. In general, the most successful of these are co-extruded multi-layer constructions.

Multi-layer compositions comprising a fluorinated polymer layer and a polyamide or polyolefin layer are known. U.S. Pat. No. 4,933,090 (Krevor), for example, discloses laminate tubular articles that can comprise layers of fluorocarbon elastomers, and PCT Publication WO 93/1493 (LaCourt) discloses a laminar film structure comprising a polyimide and a fluoropolymer. The use of fluorinated polymers in retroreflective sheeting also is known. U.S. Pat. Nos. 3,551,025 and 4,348,312, for example, describe products that include glass microspheres, and PCT WO 95/11466 and WO 95/11464 describe products containing retroreflective cube corner arrays.

A variety of methods can be used to increase the adhesion between a fluorinated polymer layer and a polyamide or polyolefin layer. An adhesive layer can, for example, be added between the two polymer layers. U.S. Pat. No. 5,047,287 discloses a diaphragm, suitable for use in automotive applications, that comprises a base fabric having bonded to at least one surface a fluororubber layer by an adhesive that includes an acrylonitrile-butadiene or acrylonitrile-isoprene rubber having an amino group.

Surface treatment of one or both of the layers also sometimes is employed to aid bonding. Some, for example, have taught treating fluoropolymer layers with charged gaseous atmosphere (*e.g.*, corona treatment) and subsequently applying a layer of a second material, for example a thermoplastic polyamide. *E.g.*, European Patent Applications 0185590 (Ueno et al.) and 0551094 (Krause et al.) and U.S. Pat. Nos. 4,933,060 (Prohaska et al.) and 5,170,011 (Martucci).

Blends of the fluoropolymer and the dissimilar layer themselves are in some cases employed as an intermediate layer to help bond the two layers together. European Patent Application 0523644 (Kawashima et al.) discloses a plastic laminate having a polyamide resin surface layer and a fluororesin surface layer. The reference recognizes the difficulties encountered when making laminates having a polyamide layer and a fluororesin layer because of the incompatibility of the two materials. The laminate of the reference is prepared by use of an intermediate layer composed of a blend of an aliphatic polyamide resin with a fluorine-containing graft copolymer.

The addition of a di- or polyamine as an auxiliary bonding agent to a "tie" layer that comprises the dissimilar, non-fluorinated polymer also has been suggested to increase the degree of chemical bonding between the fluoropolymer and the non-fluorinated layer. Such methods generally employ those fluoropolymers and non-fluorinated polymers having some measure of reactivity with the di- or polyamine to achieve an acceptable level of adhesion. Many non-fluorinated polymers that are reactive with a di- or polyamine can, however, suffer a significant change in physical properties by the amine reaction when employed to construct such tie layers; polyurethanes, for example, can suffer a significant degradation in melt viscosity in the presence of even a minimal amount of a di- or polyamine, leading to a viscosity differential between the tie-layer it comprises and the other layers that can make it prohibitively difficult to co-process the multiple layers. Another significant drawback to the use of such tie layers lies in the presence of the di- or polyamine itself. The di- or polyamine also can be a difficult material to handle directly in any process, and any method that decreases or eliminates the necessity of direct contact with a di- or polyamine presents a substantial benefit to the art. There also is an

ever-present need to expand the range of materials useful in such bonding techniques to allow for a broader, more cost effective choice of materials from which to make composite structures.

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SUMMARY OF THE INVENTION

Briefly, in one aspect, this invention provides a method of bonding fluoropolymer to substantially non-fluorinated polymeric material, the method comprising the steps of:

10 (a) blending carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefin with a suitable organic or inorganic base and an organo-onium compound that is stable in the presence of the base to form a substantially non-fluorinated polymeric material;

15 (b) providing a fluoropolymer;

(c) forming a multi-layer article comprising a substantially non-fluorinated layer made of the substantially non-fluorinated polymeric material in contact with a fluorinated layer made of the fluoropolymer and exposing the multi-layer article to
20 temperature and pressure conditions sufficient to bond the layers.

In other aspects, the present invention provides multi-layer constructions, including retroreflective sheeting, adhesive articles, and fuel-line hoses and related components, comprising multi-layer articles made according to the above-described
25 methods.

In another aspect the invention provides a bonding composition useful to adhere two dissimilar materials to one another, said composition comprising substantially non-fluorinated polymeric material that comprises a blend of carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional
30 polyolefin with a suitable organic or inorganic base and an organo-onium compound that is stable in the presence of the base.

In practice of the invention, the use of a "tie" comprising a carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefin, an organo-onium compound and an inorganic base provides a mechanism for bonding a wide array of substantially non-fluorinated polymeric materials to layers composed of fluoropolymers. The substantially non-fluorinated polymeric layers containing such a tie layer also are processable with a fluoropolymer layer and exhibit resulting physical properties that meet or exceed the properties inherent to the polymers that comprise the composite structure.

10 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Fluoropolymer materials useful in the present invention include those fluoropolymers broadly categorized structurally into two basic classes. A first class includes those thermoplastic and elastomeric fluorinated polymers, homopolymers, copolymers, terpolymers, *etc.*, comprising interpolymerized units derived from vinylidene fluoride (sometimes referred to as "VF₂" or "VDF"). Preferably fluoropolymer materials of this first class comprise at least 3% by weight of interpolymerized units derived from VF₂. Such polymers may be homopolymers of VF₂ or terpolymers and copolymers of VF₂ and other ethylenically unsaturated monomers.

20 VF₂-containing polymers and copolymers can be made by well-known conventional means, for example by free-radical polymerization of VF₂ with or without other ethylenically-unsaturated monomers. The preparation of colloidal aqueous dispersions of such polymers and copolymers is described, for example, in U.S. Pat. No 4,335,238. It follows the customary process for copolymerizing fluorinated olefins in colloidal aqueous dispersions, which is carried out in the presence of water-soluble initiators that produce free radicals, such as, for example, ammonium or alkali metal persulfates or alkali metal permanganates, and in the presence of emulsifiers, such as, in particular, the ammonium or alkali metal salts of perfluorooctanoic acid.

30 Useful fluorine-containing monomers include hexafluoropropylene ("HFP"), tetrafluoroethylene ("TFE"), chlorotrifluoroethylene ("CTFE"), 2-

chloropentafluoro-propene, perfluoroalkyl vinyl ethers, *e.g.* $\text{CF}_3\text{OCF}=\text{CF}_2$ or $\text{CF}_3\text{CF}_2\text{OCF}=\text{CF}_2$, 1-hydropentafluoropropene, 2-hydro-pentafluoropropene, dichlorodifluoroethylene, trifluoroethylene, 1,1-dichlorofluoroethylene, vinyl fluoride, and perfluoro-1,3-dioxoles such as those described in U.S. Pat. No. 4,558,142 (Squire). Certain fluorine-containing di-olefins also are useful, such as perfluorodiallylether and perfluoro-1,3-butadiene. Said fluorine-containing monomer or monomers also may be copolymerized with fluorine-free terminally unsaturated olefinic comonomers, *e.g.*, ethylene or propylene. Preferably at least 50% by weight of all monomers in a polymerizable mixture are fluorine-containing. Said fluorine-containing monomer may also be copolymerized with iodine- or bromine-containing cure-site monomers in order to prepare peroxide curable polymer. Suitable cure-site monomers include terminally unsaturated monoolefins of 2 to 4 carbon atoms such as bromodifluoroethylene, bromotrifluoroethylene, iodotrifluoroethylene, and 4-bromo-3,3,4,4-tetrafluoro-butene-1.

Commercially available fluoropolymer materials of this first class include, for example, THV 200 fluoropolymer (available from Dyneon LLC of Saint Paul, MN), THV 500 fluoropolymer (also available from Dyneon LLC), Kynar™ 740 fluoropolymer (available from Elf Atochem North America, Inc.), Fluorel™ FC-2178 fluoropolymer (available from Dyneon LLC) and those fluoropolymers sold under the "Viton" tradename by DuPont.

A second class of fluorinated material useful in the practice of the invention broadly comprises those thermoplastic and elastomeric fluorinated polymers, copolymers, terpolymers, *etc.*, comprising interpolymerized units derived from one or more of hexafluoropropylene ("HFP") monomers, tetrafluoroethylene ("TFE") monomers, chlorotrifluoroethylene monomers, and/or other perhalogenated monomers and further derived from one or more hydrogen-containing and/or non-fluorinated olefinically unsaturated monomers. Useful olefinically unsaturated monomers include alkylene monomers such as ethylene, propylene, 1-hydropentafluoropropene, 2-hydropentafluoropropene, vinylidene fluoride, *etc.*

Fluoropolymers of this second class can be prepared by methods known in the fluoropolymer art. Such methods include, for example, free-radical

polymerization of hexafluoropropylene and/or tetrafluoroethylene monomers with non-fluorinated ethylenically-unsaturated monomers. In general, the desired olefinic monomers can be copolymerized in an aqueous colloidal dispersion in the presence of water-soluble initiators which produce free radicals such as ammonium or alkali metal persulfates or alkali metal permanganates, and in the presence of emulsifiers such as the ammonium or alkali metal salts of perfluorooctanoic acid. See for example U.S. Pat. No 4,335,238.

Representative of the fluoropolymer materials of the second class are poly(ethylene-co-tetrafluoroethylene) (ETFE), poly(tetrafluoroethylene-co-propylene), poly(chlorotrifluoroethylene-co-ethylene) (ECTFE), and the terpolymer poly(ethylene-co-tetrafluoroethylene-co-hexafluoropropylene), among others; all of which may be prepared by the above-described known polymerization methods. Many useful fluoropolymer materials also are available commercially, for example from Dyneon LLC under the trade designations Hostaflon™ X6810, and X6820; from Daikin America, Inc., under the trade designations Neoflon™ EP-541, EP-521, and EP-610; from Asahi Glass Co. under the trade designations Aflon™ COP C55A, C55AX, C88A; and from DuPont under the trade designations Tefzel™ 230 and 290.

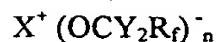
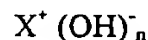
The above-described fluoropolymers may be blended with one another or blended with another fluorinated or non-fluorinated polymer to form a composite blend material useful to construct a fluorinated layer. Polyvinylidene fluoride, for example, may be blended with polymethylmethacrylate. The described fluoropolymers may also be dehydrofluorinated according to the method described in WO 98/08879.

The substantially non-fluorinated, or "tie," layer of the invention comprises, in its most essential aspect, a melt-processable, carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefin, one or more organo-onium compounds and a suitable organic or inorganic base. One or more additional non-fluorinated polymers miscible with the a melt-processable, carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefin may also be blended into the tie layer. Some amount of one or more

aliphatic di- or polyamines also may be added to the tie layer to further improve its bonding properties. The tie layer material, comprising the above components along with any additional adjuvants, may be made by melt mixing the components in accordance with conventional methods as a batch process or by a twin screw extruder as a continuous process.

The above components may be compounded together according to any conventional method, for example in a bowl mixer or other such tool, to form the substantially non-fluorinated material. Typically, the components will be compounded such that the carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefin comprises between about 80 and about 99.8 percent of the blend by weight. The organo-onium typically will comprise between about 0.1 and about 5 weight percent of the blend, and the base typically will comprise between about 0.1 and about 10 percent of the blend by weight.

Any of a broad class of organic and inorganic bases may be employed to blend with the carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefin in the manner described above. Such classes of bases include those depicted by any one of the formulas:



where:

n is 1 or 2;

X is a monovalent or divalent alkali or alkaline earth ion, preferably potassium or sodium;

R is a substituted or unsubstituted alkyl, aryl, allyl, aralkyl or arallyl group that may contain one or more catenary or noncatenary heteroatoms such as nitrogen, sulfur and oxygen, and that may contain linear or branched and cyclic or acyclic segments; R preferably contains no more than about six carbon atoms;

R_f is a partially or fully fluorinated, substituted or unsubstituted alkyl, aryl, allyl, aralkyl or arallyl group that also may contain one or more catenary or noncatenary heteroatoms such as nitrogen, sulfur and oxygen, and that may also contain linear or branched and cyclic or acyclic segments; like the above-defined R group, R_f preferably contains no more than about six carbon atoms; and

each Y is independently a hydrogen atom or is an R or R_f group as above-defined with the proviso that both Y groups are not R_f.

Other bases useful in practice of the invention include the sodium salt of 4,4'-hexafluoroisopropylidenyl bisphenol ("Na₂BF₆"), carbonate salts, and sodium sulfide.

Any among a large class of organo-onium compounds that are stable in the presence of the chosen base are useful for incorporation into the substantially non-fluorinated polymeric material. As is known in the art, an organo-onium is the conjugate acid of a Lewis base (e.g. phosphine, amine and ether) and can be formed by reacting said Lewis base with a suitable alkylating agent (e.g., an alkyl halide or acyl halide) resulting in an expansion of the valence of the electron donating atom of the Lewis base and a positive charge on the organo-onium compound. Many of the organo-onium compounds useful in the present invention contain at least one heteroatom, *i.e.*, a non-carbon atom such as N, P, O, bonded to organic or inorganic moieties. One class of quaternary organo-onium compounds particularly useful in the present invention broadly comprises relatively positive and relatively negative ions wherein a phosphorus, arsenic, antimony or nitrogen generally

comprises the central atom of the positive ion, and the negative ion may be an organic or inorganic anion (*e.g.*, halide, sulfate, acetate, phosphate, phosphonate, hydroxide, alkoxide, phenoxide, bisphenoxide, *etc.*). Because of their relative stability in the presence of most inorganic bases, phosphoniums are the most preferred organo-oniums for use in the present invention. Sulfoniums are not chemically stable in the presence of most useful organic and inorganic bases and therefore are not considered useful in the invention.

Many of the useful organo-onium compounds are described and known in the art. See, for example, U.S. Pat. Nos. 4,233,421 (Worm), 4,912,171 (Grootaert et al.), 5,086,123 (Guenther et al.), and 5,262,490 (Kolb et al.) all of whose descriptions are herein incorporated by reference. Fluorinated oniums, such as those described in U.S. Pat. No. 5,591,804 (Coggio et al.), and multifunctional oniums, such as those comprising two or more onium groups in the same molecule (*e.g.*, *bis*-phosphoniums) may also be employed. Representative examples include the following individually listed compounds and mixtures thereof:

triphenylbenzyl phosphonium chloride
tributylallyl phosphonium chloride
tributylbenzyl ammonium chloride
tetrabutyl ammonium bromide
8-benzyl-1,8-diazabicyclo [5,4,0]-7-undecenium chloride
benzyl tris(dimethylamino) phosphonium chloride
benzyl(diethylamino)diphenylphosphonium chloride

Any melt-processable, carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefin may be used to make the substantially non-fluorinated polymeric material of the invention. Polyolefins, *e.g.*, polymers of ethylene, propylene, acrylic monomers, other higher α -olefins, or other ethylenically unsaturated monomers, may be functionalized by homopolymerization of functional olefin monomers or by co-polymerization of non-functional olefin monomers with functional monomers, for example, with acrylic acid or maleic anhydride, vinyl acetate, *etc.* Polyolefins may also be modified, or functionalized, after polymerization, for example by grafting, by oxidation or by forming ionomers.

Such polymers and copolymers can be prepared by conventional free-radical polymerization or catalysis of such ethylenically unsaturated monomers. The degree of crystallinity of the hydrocarbon polymer or copolymer can vary; the polymer may, for example, be a semi-crystalline high density polyethylene or may be an elastomeric copolymer of ethylene and propylene. Representative of such substantially non-fluorinated polymer useful in the present invention include, but are not limited to, co- and terpolymers of the above-listed functional monomers with, for example, propylene, ethylene, vinyl acetate, *etc.* The carboxyl, anhydride, or imide functional polymers useful as the hydrocarbon polymer generally are commercially available. Anhydride modified polyethylenes, for example, are available commercially from the E.I. DuPont DeNemours Co., Wilmington, DE, under the trade designation "BYNEL," and useful oxycarboxy functional polyethylenes are available under the tradename "ELVAX" also available from DuPont.

Blends of one or more of the carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefins may be blended together or with other suitable polymers to find utility in forming the substantially non-fluorinated layer or layers of the invention.

The polymeric layers comprising the composite structures of the invention, including the tie layer described above, may include optional additives, such as those typically used in other thermoplastic applications. Such additional adjuvants include, for example, pigments, tackifiers, fillers, electrically conductive materials (such as those described in U.S. Patent 5,552,199), electrically insulative materials, stabilizers, antioxidants, lubricants, processing aids, impact modifiers, viscosity modifiers, as well as any appropriate mixture or mixtures thereof.

Methods known in the fluoropolymer art can be used to produce a bonded multi-layer article wherein a fluoropolymer material is in substantial contact with the substantially non-fluorinated polymeric blend material. For instance, the fluoropolymer and the substantially non-fluorinated polymeric material can be formed into thin film layers by known methods. The fluorinated layer and the substantially non-fluorinated layer can then be laminated together under heat and/or

pressure to form a bonded, multi-layer article. Alternatively, the fluoropolymer and the substantially non-fluorinated polymeric blend material, along with one or more additional layers where desired, can be co-extruded into a multi-layer article. See *e.g.*, U.S. Pat Nos. 5,383,087, and 5,284,184, whose descriptions are incorporated
5 herein by reference for such purpose.

The heat and pressure of the method by which the layers are brought together (*e.g.*, coextrusion or lamination) may be sufficient to provide adequate adhesion between the layers. It may, however, be desirable to further treat the resulting multi-layer article, for example with additional heat, pressure, or both, to
10 provide additional adhesive bond strength between the layers. One way of supplying additional heat, when the multi-layer article is prepared by extrusion, is by delaying the cooling of the multi-layer article after co-extrusion. Alternatively, additional heat energy may be added to the multi-layer article by laminating or coextruding the layers at a temperature higher than necessary for merely processing
15 the several components. Or, as another alternative, the finished multi-layer article may be held at an elevated temperature for an extended period of time. For example the finished multi-layer article may be placed in an oven or heated liquid bath or a combination of both.

Similar methods may also be employed to produce a bonded multi-layer
20 article where the substantially non-fluorinated polymeric blend material is in substantial contact with a dissimilar non-fluorinated material.

The methods of the present invention provide multi-layer articles exhibiting ease of processability and improved inter-layer adhesive bond strength between a fluorinated layer and a substantially non-fluorinated layer or between two
25 substantially dissimilar non-fluorinated layers. Multi-layer articles of the invention can have utility as films, containers, or tubing that require specific combinations of barrier properties, high and low temperature resistance, and chemical resistance. Such methods and compositions are particularly useful for making multi-layer articles comprising a fluoropolymer material suitable for use in motor vehicles, for
30 example as fuel-line hoses, and for films and blow-molded articles such as bottles, where chemical resistance and barrier properties are important.

The multi-layer articles can have two, three, or even more separate layers. For example, the present invention contemplates a multi-layer article including a fluorinated layer, a substantially non-fluorinated layer, and optionally further comprising one or more additional layers comprising fluorinated or non-fluorinated polymers. As a specific example, a bi-layer article can be prepared according to the present invention, the bi-layer article comprising a fluorinated layer and a substantially non-fluorinated layer containing the amine-functionalized base polymer, where the bonding composition is used to increase the adhesive bond strength between the two layers. One or more additional layers comprising fluorinated or non-fluorinated polymer can, either thereafter or simultaneously (*i.e.*, to form a tri-layer article), be bonded to one or more of the fluorinated layer or substantially non-fluorinated layer, to produce a multi-layer article having three or more layers.

Any appropriate fluorinated or non-fluorinated polymeric material may be utilized as an additional layer; useful among them are any of a number of well known, hydrocarbon-based polymers. Thermoplastic polyamides, polyurethanes, polyolefins, polyesters, and acrylate and methacrylate polymers and copolymers find utility in such embodiments. Any of the previously-described fluoropolymers may also be added to the multi-layer articles of the invention.

The methods of the invention prove particularly advantageous in producing a composite structures of three or more layers where at least one of the additional layers is an unfunctionalized polyolefin, *e.g.*, a linear low or high density polyethylene. Such unfunctionalized polyolefins typically are very difficult to adhere to directly or indirectly to fluorinated layers using conventional bonding methods.

Utilizing techniques of selection, a multi-layer composite article may be constructed having the combined benefits of each constituent layer. For instance, a fluoropolymer that exhibits particular advantage in bonding to a chosen substantially non-fluorinated polymeric material (such as the commercially available THV™ 200) may be used as the fluoropolymer layer immediately adjacent to the layer of substantially non-fluorinated polymer, and a fluoropolymer exhibiting relatively

superior vapor barrier properties (such as the commercially available THV™ 500) may be bonded to the immediate fluoropolymer layer. A composite so formed possesses the combined advantages of its constituent layers: superior bond strength and superior vapor barrier properties.

5 Transparent embodiments of multi-layer compositions of the present invention may find particular utility in the construction of retroreflective sheeting articles generally, and particularly when resistance to chemical agents, solvents, soiling, and/or reduced moisture vapor transmission and/or good interlayer adhesion in flexible sheetings subject to severe bending and flexing is required.

10 The compositions of this invention may be rendered retroreflective by forming retroreflective elements on one side of the composition, or alternatively, by attaching a retroreflective base sheet by means of a transparent adhesive or by direct lamination. The retroreflective base sheet may comprise a member with cube corner retroreflective elements or may comprise a microsphere-based retroreflective
15 structure, *e.g.* comprising a monolayer of transparent microspheres and reflective means disposed on the opposite side of the monolayer from the multi-layer composition. It is preferred that the base layer is disposed on a non-fluoropolymer layer of the multi-layer composition. An embodiment of this invention includes the encapsulated retroreflective sheeting article as is disclosed in U.S. Patent No.
20 3,190,178, in which the cover layer is provided by a multi-layer composition according to the present invention.

 Retroreflective articles of the invention may be made in rigid or flexible form. Multi-layer compositions of the present invention may be used as barrier layers. An embodiment of the present invention includes articles in accordance with
25 U.S. Pat. No. 5,069,964 which is incorporated herein by reference, in which the plasticizer-resistant barrier layer comprises a multi-layer composition in accordance with the present invention. The multi-layer compositions of the present invention may find particular utility in the construction of flexible retroreflective sheeting articles. A preferred embodiment of the present invention includes a retroreflective
30 article in accordance with PCT WO 95/11464 or PCT/WO 95/11943, both of which are incorporated herein by reference, wherein the flexible overlay film described in

PCT WO 95/11464 or the flexible body layer of PCT/WO 95/11943 is constituted by a multi-layer composition in accordance with the invention. Suitable fluoropolymers comprising interpolymerized units of vinylidene fluoride of the type specified for use with flexible sheeting in accordance with these two patent applications may be poly(vinylidene fluoride-co-hexafluoropropylene), for example, Kynar Flex™-2800 available from Elf Atochem North America, Inc., Philadelphia, Pennsylvania, or poly(tetrafluoroethylene-co-hexafluoropropylene-co-vinylidene fluoride), for example, THV 200 or 500. The non-fluoropolymer layer in such constructions may be any of the non-fluoropolymers specified in the above patent applications, for example, ionomeric ethylene copolymers, low density polyethylenes, polyethylene copolymers, or aliphatic or aromatic polyurethanes or similar compounds. For highly flexible products, a multi-layer composition of this invention that includes a THV layer and a polyurethane layer is particularly preferred. The microstructure elements including either solidly connected or segregated cube corners may be microreplicated, preferably onto the non-fluoropolymer layer. Alternatively, the multi-layer compositions may be adhered to microstructure elements. As will be understood, any conventional form of retroreflective microstructure elements may be used including, for example, arrays of canted, tiled, specially shaped, colored, or colorless cube corner elements.

Similarly, multi-layer compositions may be used with retroreflective sheeting products including microspheres in a base layer. Specific embodiments of the invention include retroreflective articles according to U.S. Pat Nos. 4,896,943, U.S. Pat No. 4,025,159 or U.S. Pat No. 5,066,098, all of which are included herein by reference, in which the cover film of U.S. Pat Nos. 4,896,943 or 4,025,159 or the cover sheet of U.S. Pat No. 5,066,098 is constituted by a multi-layer composition in accordance with this invention. The multi-layer compositions of the present invention further may themselves include retroreflective micro-elements, such as transparent microspheres, incorporated into the fluoropolymer or the non-fluoropolymer layer, for example in a further embodiment of the present invention, the fluoropolymer layer of a multi-layer composition according to the present invention may constitute the continuous overlaying transparent topcoat of U.S. Pat.

No. 3,551,025 which is incorporated here by reference and the non-fluoropolymer layer may constitute the binder of the same.

The adhesive articles taught by the present invention comprise an adhesive layer composed of an adhesive material disposed as the outer layer of the multilayer composite constructions already described, and such articles may find particular utility as paint replacement films. Any of a wide variety of adhesives may be usefully incorporated into such articles, including those which are thermoplastic (fusible), thermosetting (cure to a crosslinked state), or combinations of both. One particular class of adhesives are those which are pressure-sensitive in nature. That is, they display permanent and aggressive tackiness to a wide variety of substrates at room temperature. Many pressure-sensitive adhesive materials are known in the adhesive art, and those that are suitable may comprise acrylate esters, acrylamides, thermoplastic elastomers, natural rubbers, olefins, silicones, vinyl ethers, esters, urethanes, *etc.*, as well as selected polymers, and copolymers of these materials, and mixtures thereof. The actual choice of the adhesive is largely dependent on the end use to which an artisan will apply the final adhesive article. Some useful pressure sensitive adhesives are described, for example, in U.S. Patent Nos. Re. 24,906, 4,112,213, 4,323,557. Those skilled in the art will recognize that the aforementioned adhesive components might also include various chemical modifiers so as to provide utility required by a particular application; *e.g.*, tackifiers, crosslinkers, stabilizers, initiators, *etc.*

Also useful are various thermosetting adhesives that can cure, for example, upon exposure to moisture, heat, radiation, *etc.* to an infusible, crosslinked state. Useful thermosetting adhesives include those formed by addition polymerization methods from, for example, unsaturated polyesters, epoxies, urethanes, cyanoacrylates, as well as mixture of these components or polymers, copolymers, graft copolymers, and interpenetrating networks comprising these components. Further information about many different types of adhesive may be found in I. Skeist, Ed., *Handbook of Adhesives*, Third Edition, 1990.

To apply an adhesive layer to the substrate backing material, any known coating method can be used, such as gravure coating methods, spray coating

methods, die coating methods such as curtain coating and fluid bearing die methods, hot melt coating methods, *etc.* The particular method chosen can depend on the type of adhesive chosen (*i.e.*, a structural adhesive versus a pressure sensitive adhesive) as well as the chemistry of the chosen adhesive. Optionally, after the
5 adhesive is applied to the substrate, the adhesive layer can be cured by known methods such as by exposure to radiation, heat, moisture, *etc.*

Other embodiments of the adhesive articles provided herein comprise three or more additional layers, positioned on either the opposing surface of a fluorinated or substantially non-fluorinated layer, onto at least one of the outer layers of which
10 is placed an adhesive material. It will be understood that where one or more said additional layers comprise a substantially non-fluorinated polymer, that additional layer also can contain bonding composition. This would prove useful, for example, where a fluoropolymer layer is "sandwiched" between two dissimilar polymeric layers, and to bond the three layers together, both dissimilar layers contacting the
15 fluorinated layer could contain bonding composition. Additional layers may then be placed on either or both sides of such a construction.

In another specific embodiment of the invention, the adhesive article can find application as a drag reducing article such as a drag reduction film. In such an application, a fluoropolymer layer is formed into a drag reducing
20 patterned layer before, during, or after bonding to one or more layers of the article. Such a drag reducing patterned fluoropolymer layer may be prepared, for example, by extruding or coating the fluoropolymer onto a patterned sheet or roll. When the fluoropolymer is removed from the patterned sheet or roll, a surface of the fluoropolymer will be formed into a drag reducing pattern. The non-patterned
25 surface of the patterned fluoropolymer layer is bonded to other layers, including the substantially non-fluorinated layer, to produce a drag reducing adhesive article. Such a drag reducing adhesive article can reduce the resistance to drag created by a fluid (*e.g.*, air, gas, water, *etc.*) flowing across the patterned fluorinated layer. The outer, exposed surface of such an article is provided with a drag reducing pattern.
30 While a variety of waveforms may be employed to produce the patterned layer, those that are preferred typically comprise a series of essentially parallel peaks

separated by a series of essentially parallel valleys. The patterned surface may be a symmetric saw tooth pattern in which each of the peaks are identical as are each of the valleys, although parallel peaks of different heights may be separated by a series of parallel valleys. The saw tooth pattern may also comprise alternating, parallel, asymmetric peaks separated by a series of parallel, asymmetric valleys.

The dimensions of the peaks and valleys are not critical provided that whatever patterned surface is employed, it provides a desired reduction in drag. The optimum dimensions are somewhat dependent upon the speed at which the body to be covered passes through the fluid (or the speed at which the fluid passes over the body). It has been found that peaks having a height of about 10 to 250 microns (about 0.4 to 10 mils) are useful. Within this range it is preferred that the peaks be about 20 to 150 microns (about 0.8 to 6 mils) high for high speed uses (e.g., aircraft). The peak-to-peak spacing between adjacent peaks can likewise vary depending upon, for example, the application of the article. A spacing of about 10 to 250 microns (about 0.4 to 10 mils) is useful, although, for aircraft applications, a spacing of about 20 to 150 microns (about 0.8 to 6 mils) is preferred. The included angle between adjacent peaks can also vary. While flat and round bottom valleys may be useful, it is preferred that the valleys and peaks be generally V-shaped and have an included angle of from 15° to 140° , more preferably from 50° to 60° .

The drag reduction articles of the invention may readily be applied to a variety of bodies to reduce the drag experienced when that body moves through a fluid medium or when a fluid moves past the body. Preferably the article is positioned on the body such that the patterned surface will provide maximum drag reduction. When the patterned surface comprises essentially parallel peaks and valleys, maximum drag reduction is achieved when the peaks and valleys are generally parallel to the fluid flow. Bodies to which the drag reducing article may be applied include the surface of an airplane, the hull of a boat or other watercraft, the surface of the motor vehicle, or the interior surface of a fluid-conveying conduit. The patterned adhesive articles of the invention also may be used as patterned paint replacement films and may also be employed to achieve certain desired optical

effects that can be utilized to alter the appearance of the body onto which they are applied.

The following examples are offered to aid in the understanding of the present invention and are not to be construed as limiting the scope thereof.

5 Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLES

10 TEST PROCEDURES

Peel Strength

Peel strength of laminated samples was determined following the test procedures described in ASTM D-1876 entitled "Standard Test Method for Peel
15 Resistance of Adhesives," more commonly known as the "T-peel" test. Peel data was generated using an Instron™ model 1125 tester (available from Instron Corp., Canton, MA) equipped with a Sintech Tester 20 (available from MTS Systems Corporation, Eden Prairie, MN). The Instron tester was operated at a cross-head speed of 100 mm/min. Peel strength, which is reported in kg/2.54 cm width as an
20 average of at least three samples, was calculated as the average load measured during the peel test.

TIE-LAYER PREPARATIONS

25 Example 1

A tie-layer composition consisting of a mixture of Elvax™-250 (23.5 g, an ethylene/vinyl acetate copolymer available from E.I. DuPont DeNemours Co., Inc., Wilmington, DE), potassium hydroxide (1.0 g) and tetrabutyl phosphonium bromide (Onium#1, 0.5 g, available from Aldrich Chemical Co., Inc., Milwaukee, WI) was
30 compounded in a Plasticorder™ (an internal bowl mixer equipped with roller blades, available from C.W. Brabender Instruments, Inc., South Hackensack, NJ) at 200 °C for 10 minutes at a mixing rate of 60-70 revolutions per minute (rpm). After mixing, a portion of the compounded material was pressed into a 0.20 mm thick film by pressing between Teflon™ cloth at 200 °C in a Wabash Hydraulic

Press at approximately 30 KPa pressure for approximately 30 seconds. The film was cut into 1.25 cm x 5.08 cm coupons for subsequent conversion into peel test specimens.

5 **Example 2**

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax™-250 (23.5 g), potassium hydroxide (0.5 g), and tetrabutyl phosphonium bromide (0.2 g).

10 **Example 3**

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax-350 (20 g), sodium methoxide (0.25 g) and tetrabutyl phosphonium bromide (0.2 g).

15 **Example 4**

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax-350 (20 g), sodium methoxide (0.2 g) and tetrabutyl phosphonium bromide (0.2 g).

20 **Example 5**

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax-450 (20 g), cesium hydroxide (1.3 g of a 50% aqueous solution) and tetrabutyl phosphonium bromide (0.2 g).

25

Example 6

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax-450 (20 g), sodium methoxide (0.25 g) and tetrabutyl phosphonium bromide (0.2 g).

30

Example 7

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax-450 (20 g), potassium hydroxide (0.2 g) and tetrabutyl phosphonium bromide (0.2 g).

5

Example 8

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax-450 (20 g), potassium hydroxide (0.1 g) and tetrabutyl phosphonium bromide (0.1 g).

10

Example 9

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax-450 (20 g), potassium hydroxide (0.2 g) and tetrabutyl phosphonium bromide (0.1 g).

15

Example 10

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax-450 (20 g), potassium thioacetate (available from Aldrich Chemical Co., 0.6 g) and tetrabutyl phosphonium bromide (0.2 g).

20

Example 11

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax-450 (20 g), sodium trimethylsilanolate (available from Aldrich Chemical Co., 1.0 g) and tetrabutyl phosphonium bromide (0.2 g).

25

Example 12

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax-450 (20 g), sodium

30

phenoxide (available from Aldrich Chemical Co., 0.4 g) and tetrabutyl phosphonium bromide (0.2 g).

Example 13

- 5 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of AT1841 (23.5 g, an ethylene/vinyl acetate copolymer available from AT Polymer, Edmonton, Canada), potassium hydroxide (1.0 g) and tetrabutyl phosphonium bromide (0.5 g).

10 Example 14

 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of AT1841 (23.5 g), potassium hydroxide (0.2 g) and tetrabutyl phosphonium bromide (0.2 g).

15 Example 15

 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of AT1841 (23.5 g), potassium hydroxide (0.1 g) and tetrabutyl phosphonium bromide (0.1 g).

20 Example 16

 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of AT1841 (23.5 g), sodium hydroxide (1.0 g) and tetrabutyl phosphonium bromide (0.5 g).

25 Example 17

- A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-1123 (20 g, an acid modified ethylene/vinyl acetate copolymer, available from E.I. DuPont DeNemours, Inc., Wilmington, DE), potassium hydroxide (0.2 g) and tetrabutyl phosphonium
30 bromide (0.2 g).

Example 18

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g, an acid modified ethylene/vinyl acetate copolymer, available from E.I. DuPont DeNemours, Inc., Wilmington, DE), potassium hydroxide (0.1 g) and tetrabutyl phosphonium bromide (0.1 g).

Example 19

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), potassium hydroxide (0.2 g) and tetrabutyl phosphonium bromide (0.2 g).

Example 20

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), sodium phenoxide (1.0 g, available from Aldrich Chemical Co.) and tetrabutyl phosphonium bromide (0.2 g).

Example 21

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), sodium phenoxide (0.6 g, available from Aldrich Chemical Co.) and tetrabutyl phosphonium bromide (0.2 g).

Example 22

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), sodium *para*-chlorophenoxide (1.0 g, available from Aldrich Chemical Co.) and tetrabutyl phosphonium bromide (0.2 g).

30

Example 23

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), sodium trimethylsilonate (0.2 g, available from Aldrich Chemical Co.) and tetrabutyl
5 phosphonium bromide (0.2 g).

Example 24

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), sodium
10 2,2,2-trifluoroethoxide (2.0 g) and tetrabutyl phosphonium bromide (0.2 g, prepared by the reaction of 2,2,3,3,3-pentafluoropropanol with an equivalent weight of sodium methoxide at room temperature and subsequently removing the methanol in a rotary evaporator).

Example 25

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), sodium
2,2,2-trifluoroethoxide (0.5 g, prepared by the reaction of 2,2,2-trifluoroethanol with an equivalent weight of sodium methoxide at room temperature and
20 subsequently removing the methanol in a rotary evaporator) and tetrabutyl phosphonium bromide (0.2 g).

Example 26

A tie-layer composition was prepared substantially as described in Example
25 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), potassium carbonate (0.2 g) and tetrabutyl phosphonium bromide (0.2 g).

Example 27

A tie-layer composition was prepared substantially as described in Example
30 1 except that the compounding mixture consisted of Primacor™-3150 (20 g, a nominally 97/3 parts by weight ethylene/acrylic acid copolymer, nominally 97/3

wt.%, available from Dow Chemical Co., Inc., Midland, MI), sodium methoxide (0.25 g) and tetrabutyl phosphonium bromide (0.2 g).

Example 28

- 5 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3150 (20 g), potassium hydroxide (0.1 g) and tetrabutyl phosphonium bromide (0.2 g).

Example 29

- 10 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3150 (20 g), potassium hydroxide (0.2 g) and tetrabutyl phosphonium bromide (0.2 g).

Example 30

- 15 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3150 (20 g), potassium hydroxide (0.6 g) and tetrabutyl phosphonium bromide (0.2 g).

Example 31

- 20 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3150 (20 g), Na₂BF₆ salt (1.0 g, prepared by the reaction of BF₃ and two equivalents of sodium methoxide and removing the methanol on a rotary evaporator) and tetrabutyl phosphonium bromide (0.2 g).

25

Example 32

- A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3150 (20 g), sodium phenoxide (0.5 g) and tetrabutyl phosphonium bromide (0.2 g).

30

Example 33

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3150 (20 g), potassium carbonate (1.0 g) and tetrabutyl phosphonium bromide (0.2 g).

5

Example 34

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3460 (20 g, a nominally 91/9 parts by weight ethylene/acrylic acid copolymer, available from Dow Chemical Co., Inc.), potassium hydroxide (1.0 g) and tetrabutyl phosphonium bromide (0.2 g).

10

Example 35

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3460 (20 g), potassium hydroxide (0.5 g) and tetrabutyl phosphonium bromide (0.2 g).

15

Example 36

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3460 (20 g), sodium phenoxide (1.0 g) and tetrabutyl phosphonium bromide (0.2 g).

20

Example 37

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3460 (20 g), sodium 2,2,2-trifluoroethoxide (1.0 g) and tetrabutyl phosphonium bromide (0.2 g).

25

Example 38

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3340 (20 g, a nominally 93.5/6.5 parts by weight ethylene/acrylic acid copolymer, available from

30

Dow Chemical Co., Inc.), potassium hydroxide (0.5 g) and tetrabutyl phosphonium bromide (0.2 g).

Example 39

5 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of EMAC 2220 (20 g, a nominally 80/20 parts by weight ethylene/methyl acrylate copolymer, available from Chevron Chemical Co., Houston, TX), potassium hydroxide (0.2 g) and tetrabutyl phosphonium bromide (0.2 g).

10

Example 40

 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of EMAC 2220 (20 g), potassium hydroxide (0.4 g) and tetrabutyl phosphonium bromide (0.2 g).

15

Example 41

 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of EMAC 2220 (20 g), sodium phenoxide (0.5 g) and tetrabutyl phosphonium bromide (0.2 g).

20

Example 42

 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of EVAL 105 (20 g, an ethylene vinyl alcohol copolymer, available from Eval Company of Am., Lisle, IL), Na_2BF_6 salt (1.0 g) and tetrabutyl phosphonium bromide (0.2 g).

25

Example 43

 A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of EVAL 105 (20 g), potassium hydroxide (0.2 g) and tetrabutyl phosphonium bromide (0.2 g).

30

Example 44

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of AT1841 (23.5 g), potassium hydroxide (1.0 g) and tributyl methoxy propyl phosphonium chloride (Onium #2, 0.9 g, available from Dyneon Corp., St. Paul, MN)

Example 45

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of AT1841 (23.5 g), potassium hydroxide (1.0 g) and (ethylcarboxymethyl) tributyl phosphonium chloride (Onium #3, 0.5 g, available from Dyneon Corp.).

Example 46

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of AT1841 (23.5 g), potassium hydroxide (1.0 g) and tetraethyl phosphonium chloride (Onium #4, 0.5 g, available from Aldrich Chemical Co., Inc.).

Example 47

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of AT1841 (23.5 g), potassium hydroxide (0.2 g) and tetraethyl phosphonium chloride (0.2 g).

Example 48

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), potassium carbonate (0.2 g) and tetrabutyl phosphonium chloride (Onium #5, 0.2 g).

Example 49

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), potassium *tert*-butoxide (0.4 g) and tetrabutyl phosphonium chloride (0.2 g).

5

Example 50

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Bynel™-3101 (20 g), potassium *tert*-butoxide (0.4 g), potassium hydroxide (0.2 g), and tetrabutyl phosphonium chloride (0.2 g).

10

Example 51

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax™-450 (10 g), Primacor™-3340 (10 g), potassium hydroxide (0.4 g), and tetrabutyl phosphonium bromide (0.2 g).

15

Example 52

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Elvax™-450 (10 g), EMAC 2220T (10 g), potassium hydroxide (0.2 g), and tetrabutyl phosphonium bromide (0.2 g).

20

Example 53

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3150 (15 g), Morthane™ L424.167, MI+9.8, an aliphatic polyurethane, available from Morton International, Chicago, IL, 5.0 g), potassium hydroxide (0.2 g) and tetrabutyl phosphonium bromide (0.2 g).

25

30

Example 54

A tie-layer composition was prepared substantially as described in Example 1 except that the compounding mixture consisted of Primacor™-3150 (10 g), EMAC 220, 10 g), potassium hydroxide (0.4 g) and tetrabutyl phosphonium bromide (0.2 g).

Comparative Example C-1

Elvax™-250 pellets were pressed into a 0.20mm thick film by pressing between Teflon™ cloth at 200 °C for 30 seconds at approximately 30 kPa initial pressure. The resulting film was cut into 1.25 cm x 5.08 cm coupons for subsequent conversion into peel test specimens.

Comparative Example C-2

A tie-layer composition was prepared substantially as described in Example C-1 except that the compounding mixture consisted of AT1841 (23.5 g) and tetrabutyl phosphonium bromide (0.5 g).

Comparative Example C-3

A tie-layer composition was prepared substantially as described in Example C-1 except that the compounding mixture consisted of AT1841 (23.5 g) and potassium hydroxide (1.0 g).

Comparative Example C-4

AT1841 pellets were pressed into a 0.20mm thick film by pressing between Teflon™ cloth at 200°C for 30 seconds at approximately 30 kPa initial pressure. The resulting film was cut into 1.25 cm x 5.08 cm coupons for subsequent conversion into peel test specimens.

Comparative Example C-5

EVAL 105 pellets were pressed into a 0.20mm thick film by pressing between Teflon™ cloth at 200°C for 30 seconds at approximately 30 kPa initial

pressure. The resulting film was cut into 1.25 cm x 5.08 cm coupons for subsequent conversion into peel test specimens.

Peel Test Specimen Preparation

5 Peel test specimens for the tie layer compositions of Examples 1-24 and comparative Examples C-1 through C-4 were prepared by laminating a film of the tie-layer formulation to a 0.2 mm thick film of THV™ 200 (a nominally 60/20/20 parts by weight tetrafluoroethylene (TFE), hexafluoropropylene (HFP), vinylidene fluoride (VDF) terpolymer, available from Dyneon Corp.), THV™ 500 (a
10 nominally 40/20/40 parts by weight TFE/HFP/VDF terpolymer, available from Dyneon Corp.), polyvinylidene fluoride (PVDF, available from Autochem Company of Glen Rock, NJ), linear low density polyethylene (LLDPE, available from Dow Chemical, Midland, MI) or high density polyethylene (HDPE, available from Dow Chemical) as indicated in Table 1. The unbonded laminate constructions were
15 subjected to a pressure of approximately 1kgf/cm² (initial pressure) for a period of two minutes at 200°C in a Wabash Hydraulic Press. Tabs to grip the two film components of the laminate were provided by inserting a strip of silicone release paper (#7520, available from 3M Company, St. Paul, MN) between a portion of the tie-layer sheet and the THV™ 200 sheet to a depth of approximately 1.25 cm along
20 one short edge of the laminate construction to prevent the two materials from bonding together. The laminate specimens were removed from the hot laminating press after 2 minutes and immediately transferred to a second press which was maintained at room temperature to provide consistent thermal history for all test samples. T-Peel data for all samples is reported in Table 1.

25

Table 1: T-Peel Data

Ex. #	Tie Layer Composition (Composition in g)	Adhesion to Substrate (kg/2.54 cm)				
		THV TM 200	THV TM 500	PVDF	LLDPE	HDPE
1	ELVAX 250/KOH/Onium#1 (23.5/1.0/0.5)	Break ¹	3.8	0.9-1.4	5.5	5.9
2	ELVAX 250/KOH/Onium#1 (23.5/0.5/0.2)	Break ¹	1.9	-	5.5	5.5
3	ELVAX 350/NaOMc/Onium#1 (20/0.25/0.2)	0.2	4.0	-	-	-
4	ELVAX 350/NaOMc/Onium#1 (20/0.2/0.2)	-	-	0.7	-	-
4a	ELVAX 350/NaOMc/Onium#1 (20/0.25/0.2) ²	-	-	1.3	-	-
5	ELVAX 450/CeOH/Onium#1 (20/1.3/0.2)	7.0	6.9	-	-	-
6	ELVAX 450/NaOCH ₃ /Onium#1 (20/0.25/0.2)	0.2	4.8	-	-	-
7	ELVAX 450/KOH/Onium#1 (20/0.2/0.2)	5.1	Break ¹	0.7	-	-
7a	ELVAX 450/KOH/Onium#1 (20/0.2/0.2) ³	-	-	1.3	-	-
8	ELVAX 450/KOH/Onium#1 (20/0.1/0.1)	-	3.7	-	-	-
9	ELVAX 450/KOH/Onium#1 (20/0.1/0.1) ³	-	7.4	-	-	-
10	ELVAX 450/Potassium Thioacetate/Onium#1 (20/0.6/0.2)	-	0.7	-	-	-
11	ELVAX 450/Sodium Trimethylsilanolate/Onium#1 (20/0.1/0.2)	1.7	7.0	-	-	-
12	ELVAX 450/Sodium Sulfide/Onium#1 (20/0.4/0.2)	-	5.3	-	-	-
13	AT1841/KOH/Onium#1 (23.5/1.0/0.5)	3.9	2.1	0.9-1.4	5.5	5.5
14	AT1841/KOH/Onium#1 (23.5/0.2/0.2)	0.6	3.9	-	5.5	5.0

Table 1 (cont.): T-Peel Data

Ex. #	Tie Layer Composition (Composition in g)	Adhesion to Substrate (kg/2.54 cm)				
		THV™ 200	THV™ 500	PVDF	LLDPE	HDPE
15	AT1841/KOH/Onium#1 (23.5/0.1/0.1)	0.3	0.2	-	5.0	5.9
16	AT1841/NaOH/Onium#1 (23.5/1.0/0.5)	3.9	1.4	-	-	-
17	Bynel-1123/NaON/Onium#1 (20.0/0.2/0.2)	-	6.6	-	-	-
18	Bynel-3101/KOH/Onium#1 (20.0/0.1/0.1)	-	2.4	1.0	-	-
18a	Bynel-3101/KOH/Onium#1 (20.0/0.1/0.1) ²	-	2.4	4.3	-	-
19	Bynel-3101/KOH/Onium#1 (20.0/0.2/0.2) ²	-	-	2.0	-	-
20	Bynel-3101/Sodium Phenoxide/Onium#1 (20.0/1.0/0.2)	1.6	11.2	-	-	-
21	Bynel-3101/Sodium Phenoxide/Onium#1 (20.0/0.6/0.1)	1.4	2.2	-	-	-
22	Bynel-3101/Sodium <i>p</i> - Chlorophenoxide/Onium#1 (20.0/0.1/0.1)	2.8	2.5	-	-	-
23	Bynel-3101/Sodium Trimethylsilanolate/Onium#1 (20.0/0.2/0.2)	1.3	5.4	-	-	-
24	Bynel-3101/Sodium 2,2,3,3,3- Pentafluoropropoxide/Onium#1 (20.0/2.0/0.2)	0.5	5.2	-	-	-
25	Bynel-3101/Sodium 2,2,2 - Trifluoroethoxide/Onium#1 (20.0/0.5/0.2)	0.4	2.1	-	-	-
26	Bynel-3101/KOH/Onium#1 (20.0/0.1/0.1)	-	1.6	-	-	-
27	Primacor 3150/NaOCH ₃ /Onium#1 (20/0.25/0.2)	6.1	0.2	-	-	-
28	Primacor 3150/KOH/Onium#1 (20/0.1/0.2)	3.5	0.7	-	-	-
29	Primacor 3150/KOH/Onium#1 (20/0.2/0.2)	2.3	-	-	-	-

Table 1 (cont.) T-Peel Data

Ex. #	Tie Layer Composition (Composition in g)	Adhesion to Substrate (kg/2.54 cm)				
		THV™ 200	THV™ 500	PVDF	LLDPE	HDPE
30	Primacor 3150/KOH/Onium#1 (20/0.6/0.2)	5.3	2.7	-	-	-
31	Primacor 3150/Na ₂ BF ₆ Salt/Onium#1 (20/1.0/0.2)	1.4	-	-	-	-
32	Primacor 3150/Sodium Phenoxide/Onium#1 (20/0.5/0.2)	6.1	-	-	-	-
33	Primacor 3150/K ₂ CO ₃ /Onium#1 (20/1.0/0.2)	1.1	-	-	-	-
34	Primacor 3460/KOH/Onium#1 (20/1.0/0.2)	8.0	0.2	-	-	-
35	Primacor 3460/KOH/Onium#1 (20/0.5/0.2)	1.4	0	-	-	-
36	Primacor 3340/Sodium Phenoxide/Onium#1 (20/1.0/0.2)	2.0	-	-	-	-
37	Primacor 3340/Sodium 2,2,2- Trifluoroethoxide/Onium#1 (20/1.0/0.2)	2.3	-	-	-	-
38	Primacor 3340/KOH/Onium#1 (20/0.2/0.2)	2.2	0	-	-	-
39	EMAC-2220/KOH/Onium#1 (20/0.2/0.2)	0.2	5.0	-	-	-
40	EMAC-2220/KOH/Onium#1 (20/0.4/0.2)	-	6.3	-	-	-
41	EMAC-2220/Sodium Phenoxide/Onium#1 (20/0.5/0.2)	8.1	8.7 (break)	-	-	-
42	EVAL/Na ₂ BF ₆ Salt/Onium#1 (20/1.0/0.2)	High	High	-	-	-
43	EVAL/KOH/Onium#1 (20/0.2/0.2)	17.0	-	-	-	-
44	AT1841/KOH/Onium#2 (23.5/1.0/0.9)	4.7	2.9	-	4.1	3.6
45	AT1841/KOH/Onium#3 (23.5/1.0/0.5)	High	1.6	-	-	-
46	AT1841/KOH/Onium#4 (23.5/1.0/0.5)	>5.9	>5.9	-	7.1	6.1

Table I (cont.): T-Peel Data

Ex. #	Tie Layer Composition (Composition in g)	Adhesion to Substrate (kg/2.54 cm)				
		THV™ 200	THV™ 500	PVDF	LLDPE	HDPE
47	AT1841/KOH/Onium#4 (20/0.2/0.2)	0	1.6	-	5.5	5.9
48	Bynel-3101/KOH/Onium#5 (20.0/0.2/0.2)	1.8	7.4	-	-	-
49	Bynel-3101/Potassium <i>t</i> - Butoxide/Onium#2 (20.0/0.4/0.2)	-	4.8	0.5	-	-
50	Bynel-3101/Potassium <i>t</i> - Butoxide/KOH/Onium#2 (20.0/0.4/0.2/0.2)	6.2	12.8	-	-	-
51	ELVAX450/PRIMACOR 3340/KOH/Onium#1 (10/10/0.4/0.2)	.5	2.3	-	-	-
52	ELVAX450 /EMAC2220T/KOH/Onium#1 (10/10/0.2/0.2)	0.5	4.9	-	-	-
53	Primacor-3150/Morthane L424/KOH/Onium#1 (15.0/5.0/0.2/0.2)	1.7	10.4	-	-	-
54	Primacor 3150/EMAC 2220T/ KOH/Onium#1 (10.0/10.0/0.4/0.2)	5.5	-	-	-	-
C-1	Elvax™ 250	0	0	-	-	-
C-2	AT1841/Onium#1 (23.5/0.5)	0	0	-	-	-
C-3	AT1841/KOH (23.5/1.0)	0	0	-	-	-
C-4	AT 1841	0	0	-	-	-
C-5	EVAL 105	1.6	0.2	-	-	-

1. Substrate failure, no adhesive failure observed.
2. Laminated at 230 °C.
- 5 3. Laminated at 180 °C.

Example 55

A tie layer composition was prepared using a twin screw extruder instead of a Brabender batch mixer as shown in the above examples. A Haake conical intermeshing counter rotating twin screw extruder was used. The temperature profile for each zone was: zone 1 – 25 °C; zone 2 – 170 °C; zone 3 – 200 °C; zone 4 – 200 °C. Bynel™ 3101 containing 1.5 wt % KOH was fed into a hopper and a 2.5 mm diameter strand was extruded into an ice water bath at 70 rpm and was pelletized and dries overnight at approximately 65 °C. Tetrabutyl phosphonium bromide (1 wt %) was added to the pellets and the mixture was again extruded and pelletized under the same conditions. The tie layer composition was evaluated in laminate constructions as described in Example 1, giving peel adhesion values of 3.9 kg/ 2.54 cm for THV 200 and 12.6 kg/2.54 cm for THV 500.

Various modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not limited to the illustrative embodiments set forth herein.

CLAIMS

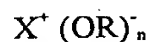
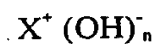
We Claim:

- 5 1. A method of bonding fluoropolymer to substantially non-fluorinated polymeric material, the method comprising the steps of:

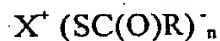
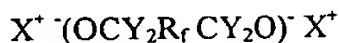
(a) blending carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefin with base and organo-onium compound that is
 10 stable in the presence of the base under processing conditions to form substantially non-fluorinated polymeric material where the base is selected from the group consisting of:

(1) those bases represented by the formulas:

15



20



where:

25

n is 1 or 2;

X is a monovalent or divalent alkali or alkaline earth ion;

R is a substituted or unsubstituted alkyl, aryl, allyl, aralkyl or arallyl group that may contain one or more catenary or noncatenary heteroatoms such as nitrogen, sulfur and oxygen, and that may contain linear or branched and cyclic or acyclic segments; R preferably contains no more than about
5 six carbon atoms;

R_f is a partially or fully fluorinated, substituted or unsubstituted alkyl, aryl, allyl, aralkyl or arallyl group that also may contain one or more catenary or noncatenary heteroatoms such as nitrogen, sulfur and oxygen, and that may also contain linear or branched and cyclic or acyclic segments;
10 like the above-defined R group, R_f preferably contains no more than about six carbon atoms; and
each Y is independently a hydrogen atom or is an R or R_f group with the proviso that both Y groups are not R_f.

15 (2) sodium salt of 4,4'-hexafluoroisopropylidenyl bisphenol, carbonate salts, and sodium sulfide;

(b) providing fluoropolymer;

20 (c) forming a multi-layer article comprising a substantially non-fluorinated layer made of the substantially non-fluorinated polymeric material in contact with a fluorinated layer made of the fluoropolymer and exposing the multi-layer article to temperature and pressure conditions sufficient to bond the layers.

25 2. The method of claim 1 further comprising the step of applying at least one additional layer to at least one side of the resulting multi-layer composition.

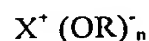
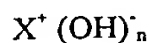
3. A multi-layer article comprising:

(a) a first layer comprising fluoropolymer; and
30 (b) a second layer comprising substantially non-fluorinated polymeric material comprising carboxyl, anhydride, imide, or acid functional polyolefin, base,

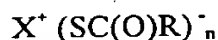
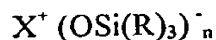
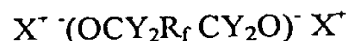
and organo-onium compound that is stable in the presence of the base, wherein said base is selected from the group consisting of:

(1) those bases represented by the formulas:

5



10



where:

15

n is 1 or 2;

X is a monovalent or divalent alkali or alkaline earth ion;

R is a substituted or unsubstituted alkyl, aryl, allyl, aralkyl or arallyl group that may contain one or more catenary or noncatenary heteroatoms such as nitrogen, sulfur and oxygen, and that may contain linear or branched and cyclic or acyclic segments; R preferably contains no more than about six carbon atoms;

20

R_f is a partially or fully fluorinated, substituted or unsubstituted alkyl, aryl, allyl, aralkyl or arallyl group that also may contain one or more catenary or noncatenary heteroatoms such as nitrogen, sulfur and oxygen, and that may also contain linear or branched and cyclic or acyclic segments; like the above-defined R group, R_f preferably contains no more than about six carbon atoms; and

25

each Y is independently a hydrogen atom or is an R or R_f group with the proviso that both Y groups are not R_f.

(2) sodium salt of 4,4'-hexafluoroisopropylidenyl bisphenol, ammonium carbonate,
5 and sodium sulfide;

and wherein said first and said second layers are bonded to one another.

4. The article of claim 3 further comprising at least one additional layer on at
10 least one side of said article.

5. The article of claim 3 or 4 further comprising adhesive material disposed on at least one outer surface of the article.

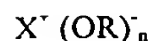
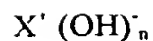
15 6. The article of claim 3, 4 or 5 wherein said article is a tape product, drag reduction film, paint replacement film, hose, container, or comprises a retroreflective base sheet.

7. The method or article according to any of the preceding claims wherein said
20 organo-onium compound is a phosphonium or ammonium compound.

8. The method or article according to any of the preceding claims wherein said base is selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium methoxide, cesium hydroxide, potassium thioacetate, sodium
25 trimethylsilanolate, sodium phenoxide, sodium *para*-chlorophenoxide, sodium 2,2,2-trifluoroethoxide, potassium *tert*-butoxide.

9. The method or article according to any of the preceding claims wherein said substantially non-fluorinated polymeric material further comprises one or more
30 additional non-fluorinated polymers miscible with the substantially non-fluorinated polymeric material.

10. The method or article according to any of the preceding claims wherein said fluoropolymer is a homopolymer of vinylidene fluoride; a copolymer or terpolymer derived vinylidene fluoride and one or more monomers selected from the group
5 consisting of tetrafluoroethylene, and hexafluoropropylene; or comprises interpolymerized units derived from monomers comprising one or more hexafluoropropylene, tetrafluoroethylene, and chlorotrifluoroethylene monomer and one or more non-fluorinated olefinically-unsaturated monomer.
- 10 11. The method or article according to any of the preceding claims wherein said fluoropolymer is blended with at least one additional polymer comprising polymethylmethacrylate.
12. The method or article according to any of the preceding claims wherein said
15 substantially non-fluorinated polymeric material comprises a blend of two or more carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefins or comprises a blend of polyolefin and carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefin.
- 20 13. A bonding composition comprising substantially non-fluorinated polymeric material comprising a blend of carboxyl, anhydride, imide, or oxycarboxy functional polyolefin with a suitable organic or inorganic base and an organo-onium compound that is stable in the presence of the base.
- 25 14. A multi-layer article comprising:
(a) a first layer comprising substantially non-fluorinated polymeric material comprising carboxyl, anhydride, imide, or acid functional polyolefin, base, and organo-onium compound that is stable in the presence of the base, wherein said base is selected from the group consisting of:
30 (1) those bases represented by the formulas:



where:

10 n is 1 or 2;

X is a monovalent or divalent alkali or alkaline earth ion, preferably potassium or sodium;

R is a substituted or unsubstituted alkyl, aryl, allyl, aralkyl or arallyl group that may contain one or more catenary or noncatenary heteroatoms such as nitrogen, sulfur and oxygen, and that may contain linear or branched and cyclic or acyclic segments; R preferably contains no more than about six carbon atoms;

15 R_f is a partially or fully fluorinated, substituted or unsubstituted alkyl, aryl, allyl, aralkyl or arallyl group that also may contain one or more catenary or noncatenary heteroatoms such as nitrogen, sulfur and oxygen, and that may also contain linear or branched and cyclic or acyclic segments; like the above-defined R group, R_f preferably contains no more than about six carbon atoms; and

20 each Y is independently a hydrogen atom or is an R or R_f group as above-defined.

(2) sodium salt of 4,4'-hexafluoroisopropylidenyl bisphenol, ammonium carbonate, and sodium sulfide; and

(b) a second layer comprising a dissimilar polymeric material wherein said first and said second layers are bonded to one another.

5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 98/17556

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08J 7/12, C08J 5/12, B32B 27/08, B32B 7/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08J, C09J, B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CAPLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E, A	EP 0873759 A2 (SCHNEIDER (USA) INC.), 28 October 1998 (28.10.98), Claims	1-14
P, A	WO 9808879 A1 (MINNESOTA MINING AND MANUFACTURING COMPANY), 5 March 1998 (05.03.98), abstract	1-14
A	EP 0637509 A1 (NITTA MOORE COMPANY), 8 February 1995 (08.02.95), abstract, claims	1-14
A	US 5047287 A (NORIYUKI HORIUCHI ET AL), 10 Sept 1991 (10.09.91), abstract	1-14

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

22 December 1998

Date of mailing of the international search report

15.02.99

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 98/17556

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>File WPI, Derwent accession no. 97-016179, Mitsubishi Chem Corp: "Laminates used for films, packing or electronic device housing - consisting of olefin layer and fluoro-resin layer bonded with adhesiv polymer compsn. prepd. from acrylate by and olefinic resin;" & JP,A,8281884, 961029, DW9702</p> <p>-- -----</p>	

S, 07967

INTERNATIONAL SEARCH REPORT
Information on patent family members

01/12/98

International application No.

PCT/US 98/17556

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0873759 A2	28/10/98	AU 6361598 A	29/10/98
WO 9808879 A1	05/03/98	AU 1464697 A	19/03/98
EP 0637509 A1	08/02/95	JP 7096564 A	11/04/95
US 5047287 A	10/09/91	JP 1177447 A	13/07/89

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